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## REVIEW

# Possible domestication of uranium oxides using biological assistance reduction



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### KEYWORDS

Uranium;  
 Nanoparticles;  
 Bio-respiration intervention;  
 Bio-reduction;  
 Structural characterization

**Abstract** Uranium has been defined in material research engineering field as one of the most energetic radioactive elements in the entire Mendeleev periodic table. The manipulation of uranium needs higher theories and sophisticated apparatus even in nuclear energy extraction or in many other chemical applications. Above the nuclear exploitation level, the chemical conventional approaches used, require a higher temperature and pressure to control the destination of ionic form. However, it has been discovered later that at biological scale, the manipulation of this actinide is possible under friendly conditions. The review summarizes the relevant properties of uranium element and a brief characterization of nanoparticles, based on some structural techniques. These techniques reveal the common link between chemical approaches and biological assistance in nanoparticles. Also, those biological entities have been able to get it after reduction. Uranium is known for its ability to destroy ductile materials. So, if biological cell can really reduce uranium, then how does it work?

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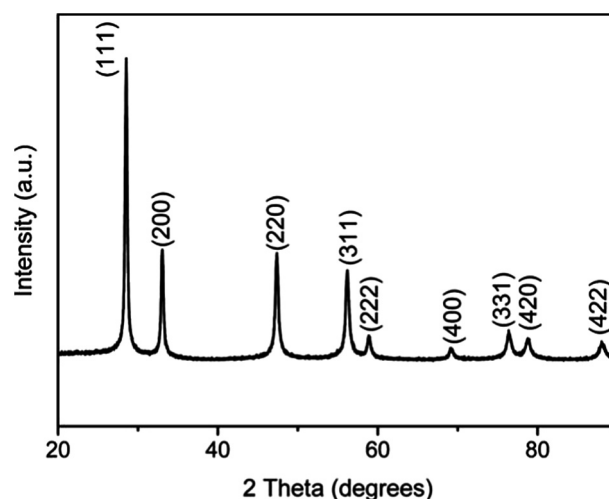
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## 1. Introduction

The synthesis of organic and inorganic materials has been related to the mastery of matter and fire (Livage, 1977). Humanity had discovered the natural fire in earliest times after the Stone Age, and since late of the Glass Age (2500 years BC), human beings have been coining the idea to manipulate the natural fire in primitive ways. During Bronze Age (2200–750 years BC) and Iron Age (750–50 years BC) metals were melted. Controlling the temperature was a serious issue, while purifying some metals. The temperature here was less than 3000 °C (Rees, 1993). Fire was used to sculpt and modify the texture and smoothness of the surface. It was not until the late ages that humanity was able to use chemical fire with more mastery over fire. This was made possible by controlling more matter twice using temperature and by the introduction of equation methods (Crosland et al., 1959). Many hybrids and composites between some specific metals became possible. One step needed more than 10,000 °C, the “chemists” could then design the materials at this level with large possibility of combinations. It has only been no more than 150 years that nuclear fire was discovered. This type of energy needed a strong theory, materials and methods to manipulate the energy at this scale. Then it has also opened the possibility of creating new isotopes, which has never existed before in the nature. Amidst all this dynamic discovery of manipulation of the matter– with use of more pressure and temperature, to shift and control various energy levels, in the living world– the entities have a strong ability to calmly manipulate different levels of energy to control and master the materials in peaceful ways. Using methods which work under physiological conditions and creating a veritable art, from difficult reactions the veritable art becomes the inspiration to sculpt and develop materials (Nassif and Livage, 2011). Many reactions were possible within micro-organisms at low temperature and pressure, however with conventional chemistry methods it needed several conditions. It was eventually concluded that inside the physiological conditions there was other chemistry that had been taking place much earlier than the beginning of the life on this planet. Green chemistry has become a technical word, referring to the low temperature and low pressure conditions of reactions, generally inspired from the methodology prevailing at that natural and/or biological scale.

Many elements are manipulated by microorganisms for their energy needs and it consists of shifting the ionic valence to create balance in global charge and the correction of the

concentration distribution between different compartments of the cell to create a dynamic equilibrium responsible for the life of the cell. Many other elements are present in the environment but they are lethal for the cell which can end the living entity even in low concentration. As they have other non desirable properties, however the same consequence can be obtained with higher concentration of the main elements. Especially metallic atoms are so highly active in terms of oxido-reduction, the studies were concerned with the effects of concentrations of many metals on the biology of cells (Nies, 1999). Microorganisms developed in a preexisting system, from the capacity to manipulate exogenous amount of metals to be protected from the ionic forms. Ions are competitive and with various affinities can interfere with the vital metabolism of the cell and create dangerous situations. For that it is wise to shift this form to less competitive and if possible the new form can be used for other new ability. For instance, as regards the bacteria discovered by Blackmore in 1975 in some place with higher concentration of iron, the bacteria synthesize iron nanoparticles to minimize the internal amount of ionic form and synthesize the iron nanoparticles with a simple methodology, that can distribute it in the cell edifices before assisting it to be orientated in magnetic field in which it lives (Blakemore, 1975). Other elements like gold,



**Figure 1** XRD pattern prototype of  $\text{UO}_2\text{NPs}$  (from Wang et al., 2008).

and silver are also manipulated by various microorganisms to get nanoparticles (Sadowski, 2010). In this paper we would concentrate on uranium element, having a particular property. This precious element has the capacity to naturally emit radiation. The main concern is to turn around the possibility of manipulating uranium at aqueous chemical scale before the destruction of the natural bioreactors and discovery of the methods to shift easily the ionic form to get more stable oxydoreductive form like nanoparticles.

As the paper will focus on the synthesis of uranium nanoparticles by an assisted biological or naturally methods, the study will be based on some relevant techniques to investigate the presence of uranium nanoparticles by a brief structural identity of the phase given by XRD, UV-Vis, FTIR and microscopy techniques and brief inventories of microorganisms methods and plants capable to synthesize uranium nanoparticles.

## 2. Physico-chemical proprieties of uranium

### 2.1. Chemical characteristics of uranium

Uranium is a pyrophoric element and the most radioactive actinide element in Mendeleev periodic table, it was discovered by Klaproth in 1789 and the name Uranium was inspired from the new discovered planet Uranus. The natural emission of uranium was unknown till the coming of Becquerel, who discovered the radioactivity of the element. Three natural nuclides for Uranium,  $^{234}\text{U}$ ,  $^{235}\text{U}$  and  $^{238}\text{U}$  are characterized the second one is almost 99.275% of natural uranium and it exists between 0.5 and 0.4.7 ppm in the common rock type.  $^{235}\text{U}$  can be fissioned and has a capacity to precede a nuclear chain reaction when it receives a right quantity of energy given by  $\alpha$ -radiation (Keith et al., 2013).

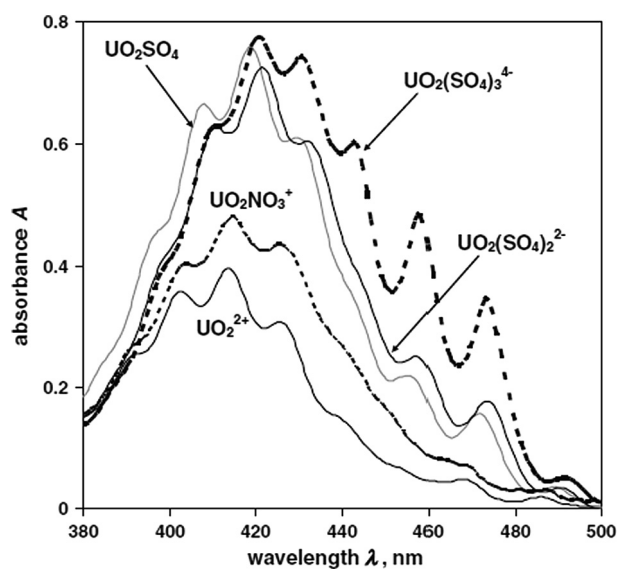
Uranium atom has a complete Radon electronic configuration (with his 86 electrons) associated with 6 other electrons distributed in three orbitals 5f, 6d and 7s. The configuration

can be written in  $[\text{Rn}] 5f^3 6d^1 7s^2$  that makes the 92 electrons a well stable distributed configuration with 6 electrons in a valence state, till the study of Weigel in 1986; the valence 0 was discovered in metallic state and then only +III and +IV are discovered and manipulated (Weigel, 1986).  $\text{U}^{\text{IV}+}$  and  $\text{U}^{\text{VI}+}$  are relatively stable (Wang et al., 2015). In the tetravalent state uranium is poorly soluble in water but only in the hexa-valent state it becomes soluble and can be explored in aqueous chemistry. Uranium can be reduced by iron salt that becomes a source of electrons responsible for the reduction. Many other sources of electrons can produce the reduction of the ions form and shift the valence state.

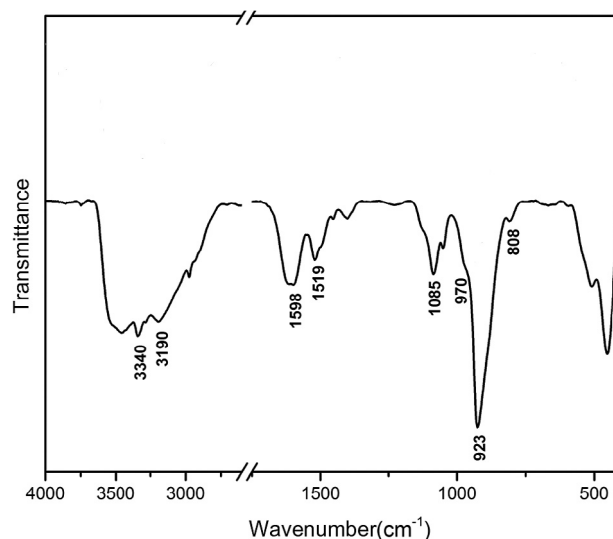
### 2.2. XRD patterns

As shown in Fig. 1, the XRD pattern of U-NP is indexed typically to the face-centered cubic- $\text{UO}_2$  (Wang et al., 2008).  $\text{UO}_2$  is the pattern displaying nine peaks, four among them were fundamentals to identify the right structure, the first two  $hkl$  plans are assigned to (111) and (200) reflections situated at  $28^\circ$ , and  $34^\circ$  respectively with the relative comparative intensity around 38%. The plan situated at  $47^\circ$  was indexed to (220) at the same relative intensity with (200). The fourth preponderant peak corresponds to (311)  $hkl$  plan situated at  $56^\circ$  (Chave et al., 2010). Five other peaks can also be present and they depend on the crystalline condition and phases.

Various other crystalline phases of uranium can be obtained depending on the synthesis conditions. For instance, in the case of  $\text{U}_3\text{O}_8$  it can be obtained by a mixed-valent uranium  $\text{U}^{+\text{V}}$  with  $\text{U}^{+\text{IV}}$  in a molar ratio of 2:1 (Selbin and Ortego, 1969) and the obtained compound crystallizes into three different polymorphs: conventional orthorhombic  $\alpha$ - $\text{U}_3\text{O}_8$  and two high-temperature modifications (hexagonal  $\text{U}_3\text{O}_8$  and orthorhombic  $\beta$ - $\text{U}_3\text{O}_8$ ) (Hoekstra et al., 1961). Some conditions of this experience matched well with physiological conditions, especially the pH, which suggests that biological entities can reduce uranium to some extent.



**Figure 2** Individual UV-vis spectra of significant U(IV) species in (sulfate-nitrate system) solution (from Vopálka et al., 2010).



**Figure 3** FT-IR spectra of the precursor for  $\text{UO}_2$  nanospheres (modified, Zhao et al., 2014).

### 2.3. UV-Vis

The UV-Vis spectra of uranyl can be recorded between 380 and 500 nm, the main absorbance peaks are present in this domain. Depending on the solution, it is possible to conclude that uranium absorbs at wavelength near to 400 nm. In the sulfate nitrate system,  $\text{UO}_2^{2+}$  can be identified by the absorbance peaks at 403, 415 and 428 nm as shown in Fig. 2, (Vopálka et al., 2010), these main peaks can be shifted and modified in the presence of different systems as sulfate or nitrate, the obtained uranyl associated with these various anions become  $\text{UO}_2\text{SO}_4$ ,  $\text{UO}_2\text{SO}_4^{4-}$ ,  $\text{UO}_2\text{SO}_4^{2-}$  and  $\text{UO}_2\text{NO}_3^+$ . The study can be taken like a model to domesticate uranyl by bacterial assistance and plant derivatives to synthesize uranium nanoparticles in the presence of molecular species present inside the biological cells when this element is preponderant in the biological mediums.

### 2.4. Infrared model spectrum

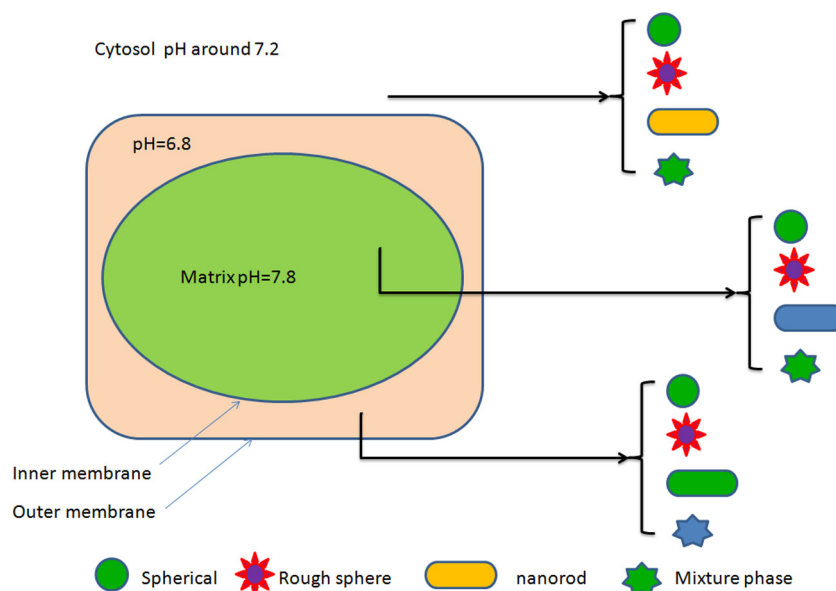
The IR spectrum given in Fig. 3 exhibits vibration bands corresponding, in addition, to the uranium the hydrazine molecules a spectators compound in the protocol of synthesis, but the representative peaks of the uranium were given by the asymmetric and symmetric stretching frequency appears respectively at  $923$  and  $808\text{ cm}^{-1}$  for U-O-U (Zhao et al., 2014). The peaks at  $3340$  and  $3190\text{ cm}^{-1}$  are assigned to the N-H stretching vibration due to the presence of the impurities, however the O-U-O or other structure present in the main structure of U-NPs is not clear and not reported.

The important point in the IR spectrum of uranium nanoparticles can be different according to the researching phase  $\text{UO}_2$ ,  $\text{U}_3\text{O}_8$  and other formula which depend on the molecular species present in the solution.

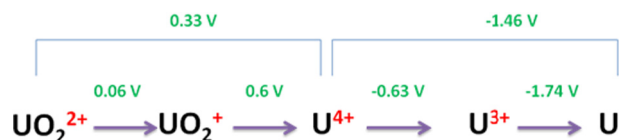
### 2.5. Microscopic analysis

It is expected that under green condition reigns in biological cells, each nanoparticle can take a particular shape. The special shape is quite related to the pH of the cell compartment within it. As there are no published studies which conclude about the relation between the specific condition of the different cell compartments and nanoparticles shapes, we will simulate the study referring to the relations between the shape and the pH given by conventional chemical reactions using SEM micrographs of representative uranium nanoparticles in order to understand well, the potential biosynthesized nanoparticles, their shapes and pH relationship depending of the locality of it synthesis.

The study of the pH influence on uranium nanoparticles size and shape done by Zhao and his collaborators (Zhao et al., 2014) lend for the evidence that the shapes and the pH directly related and the pH can define the shape as it appears in the SEM images for  $\text{UO}_2$  face-centered cubic system and/or  $\text{U}_3\text{O}_8$  which is crystallized in cubic system. The derivative shapes are in rod-shape at pH 5, when the pH takes a value near to 6, a mixture of  $\text{UO}_2$  and  $\text{U}_3\text{O}_8$  nanoparticles appear with irregular morphologies, the monodisperse and spherical shape can then be obtained in case of  $\text{UO}_2$  in case of alkaline pH starting for pH 7 and when the alkalinity grows up to 12 value of pH the structure will take an irregular form with rough surfaces. This study fits the hypothesis that the shape of uranium nanoparticles relates with some particular cell compartments; it is according to pH standard values that makes it possible to match the shape with the right compartment, for instance in mitochondria matrix the pH value is calculated at 7.8 (Porcelli et al., 2005) as pH is crucial in controlling the size and especially the shape of nanoparticles we can conclude the predominant potential shape which can be in a spherical one however in this pH it is possible to see



**Figure 4** Simulation of the potential existing uranium nanoparticles made in different locales in the cells respecting the pH value (Colors significations; Green = possible, Red = not allowed, yellow = possible in second order and bleu difficult to conclude about his presence).



**Figure 5** Oxydoreduction potentials of uranium in neutral solvent and at room temperature (from Madic et Genet, 2001).

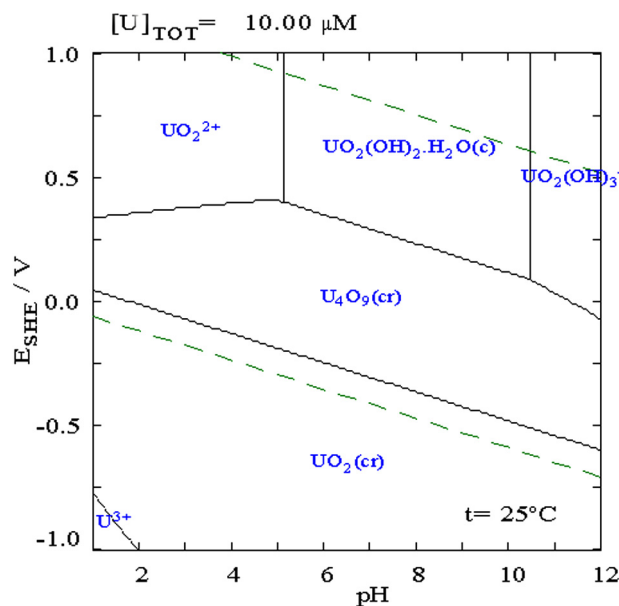
a mixture phase as  $\text{UO}_2$  and  $\text{U}_3\text{O}_8$ . At the intermembrane mitochondrial space the pH value was given by Santo-Domingo and Demareux (2012), at 6.8 which conforms to the pH-condition of nanorod structure and possible spherical shape also, the cytosolic compartment with pH under 7 and 7.4 (Roos and Boron, 1981) authorizes the spherical monodisperse features. Fig. 4 summarizes the correspondence revealed by corresponding the shape and the standard value of pH in cell compartment related to the respiration. It is also important to highlight that outside the cell the pH is still controlling the destination of the aggregation of primary nanoparticles, besides the cytosolic membrane the cell liberates various kinds of substances that can acidify or alkalize the extracellular medium and other new shapes can take place as the rough surface nanoparticles known by their appearance only in extreme value of pH. To conclude over the relationship between the locality and the shapes, it is important to draw that those nanoparticles were not in uniform shape and the shape evaluates with respect to the pH than depending on consequence to the synthesis locality in the cell.

### 3. Synergy between uranium proprieties and biological ability to reduce metals

#### 3.1. Related chemical of uranium with biological conditions

Uranium in solution is an element able to make genesis of various oxides  $\text{U}_x\text{O}_y$ , due to its higher electro-positivity. It even has the ability to react with oxygen and any other electronegative atoms. For that, the study of the system in neutral solvents like  $\text{HClO}_4$  can be taken like a model to decide the behavior of uranium nanoparticles with the potential, using the Nernstian approach. Various oxydoreduction levels are revealed and can be schematized in the figure below as mentioned by Madic and Genet (2001) and summarized in (Fig. 5).

With different potential, it is possible to see the linkage of uranium with oxygen to get the key structure for the manipulated into “friendly” condition, the nucleus is the key with valences depending on the potential, U valence 0 can lose three electron at 1.74 V and becomes oxidized at +III valence state at this order under 0.63 V will be shifted to +IV, the global changing from U to  $\text{U}^{+IV}$  can be done at 1.46 V. At that last valence uranium becomes easily associated with oxygen to reduce the instable valence and minimize the reduction ability by making the first nucleus  $\text{UO}_2^+$  and  $\text{UO}_2^{2+}$  the two starting states can be in a transition level and makes the exploration possible by a biological shifting to nanoparticles as an oxide forms of uranium as the oxygen and other near atoms like sulfur were preponderant in mitochondria matrix. With the elementary potentials, uranium nanoparticles can be produced

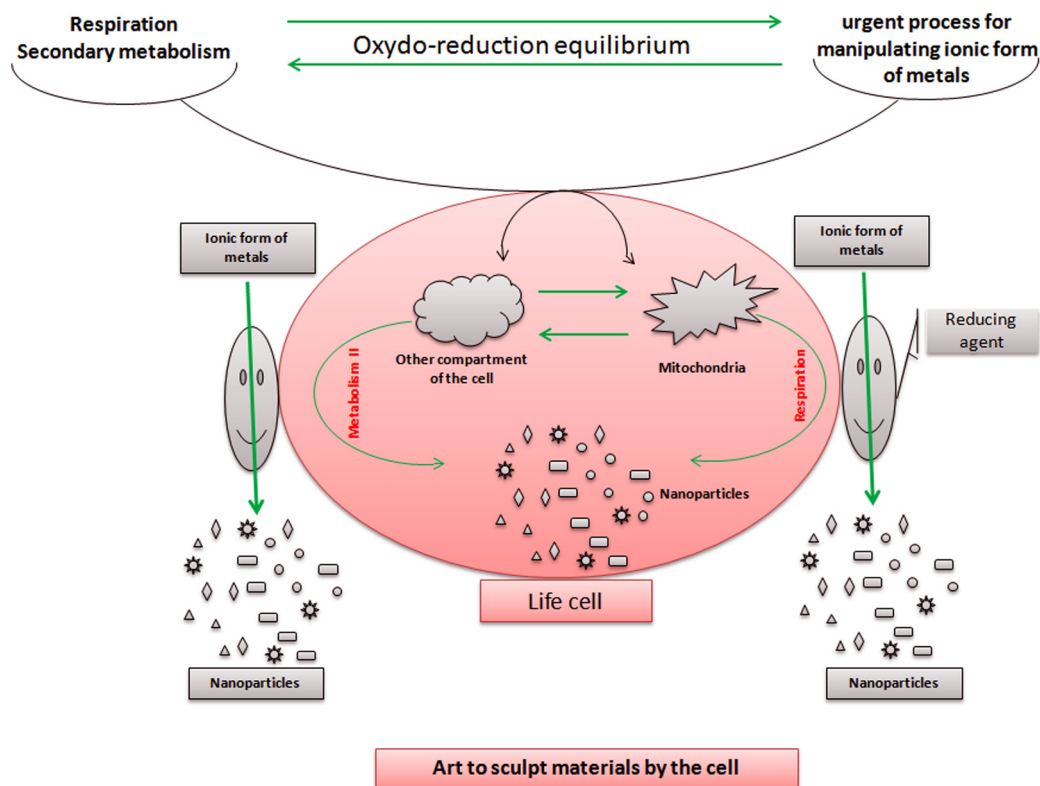


**Figure 6** Pourbaix diagram of uranium (Ignasi Puigdomenech, 2004) (Ignasi Puigdomenech, 2004).

at the condition existing in the biological cells the repartition of the ions from outside to inside the whole cell and around each cell compartment especially as these potentials are defined and present no harmful conditions to the cell. Mitochondria can be a cell reactor and the theater of balancing the charge of each element as it contains various ionic transporters and can use the high energetic element to an exploitable state and the same potential are possible and explored by the cell itself; it is one of the crucial common parameters between the conventional methods and biorespiration process. The phototrophic plants have a specialized system for photon interception and energy exploration and the iron balanced the electrons from the valence +III to +II by different reactions and combination with oxygen or other final electron receptors like Sulfur in case of some other microorganisms having S-respiration final acceptor of electrons.

After checking the relationship between the existing form of uranium and the potential conditions it is possible to match these forms with some locality in the cell as the potential master the form, it becomes then possible to manipulate the element inside the cell and shift the form to synthesize various nanoparticles. Carefully, cell can be made from this radioactive element some crystals and store in its heard a respectful amount of it. The whole plants and/or the whole cell of microorganisms comes to be used like a natural collector of uranium element from the ore places and accumulate, manipulate and aggregate it in one crystal package having the complete nuclear proprieties with the most safe chemical way. Moreover, the proprieties related to potential context of the uranium make from the biological cell a possible reactor to shift the uranium with various valences, as it is highly related to the pH the potential still not well separated from the disturb ion in biological entities that make from a pH and the difference in potential a good players to confirm the final destinies of each ion.





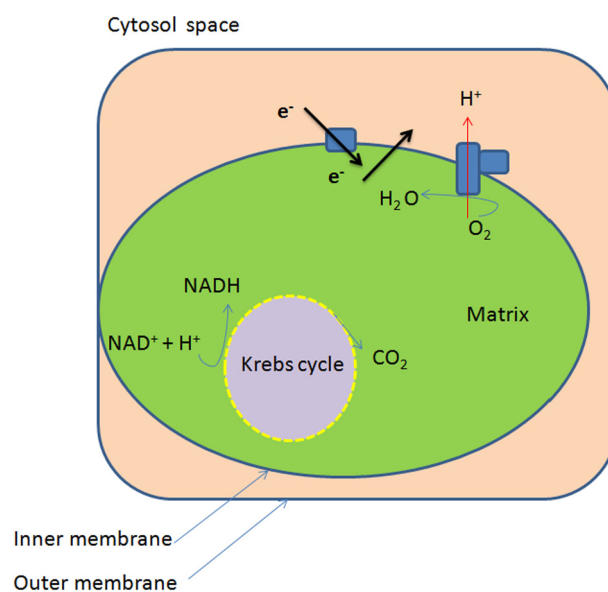
**Figure 7** Biological cell assistance ways for manipulation of ionic form of uranium.

### 3.2. Condition related to potential and pH together for shifting the forms

The pH alone plays a crucial role for the oriented nanoparticles aggregation, the growth and the structure destination, it is the case of  $\text{UO}_2$  primary nuclei derived nanoparticles. Fig. 6 presents the relationship between pH and generated potential, which is the thin thread to make the analogy with the metabolism of the cells and especially the respiration process.

The modulation of pH as a function of potential, in this context governs the specification of uranium destination from ionic state with valence III at  $-1\text{ V}$  in pH less than 2 to crystalline form given in these formula,  $\text{UO}_2$  and  $\text{U}_4\text{O}_9$  independently of the pH it is just the potential how interfere this modulation in the crystal different states (Kertes and Guillaumont, 1985). It is only up to  $0.5\text{ V}$  that pH restarts mastering the association of the main nucleus  $\text{UO}_2^{2+}$  in acid pH this is the predominant phase, the association with hydroxides becomes relevant at neutral value till the high alkaline values the dominant phase becomes  $\text{UO}_2(\text{OH})_3^+$ , this transition phases go well with pH modulation even potential in the biological cells. To respire cell use its ability to modify continually a dynamic equilibrium to maintain the difference distribution of various ionic species like  $\text{H}^+$  and  $\text{OH}^-$  to modulate pH when it is necessary, by this way it becomes possible to manipulate the destination of uranium as its different valence which can be including in a right stoichiometric phases. The relevant study in this context was given by Notz et al. at higher temperature (Notz et al., 1962) and the model of reduction suggests at least five phases arranged in sequence starting from the most

stable allotrope which is  $\gamma\text{-UO}_3$  (orthorhombic), to  $\text{U}_3\text{O}_8$  (hexagonal),  $\text{U}_3\text{O}_8$  (orthorhombic)  $\text{UO}_2^+$  (cubic) and  $\text{UO}_2$  (cubic) all these different phases can take place by mastering of potential, valence charges, eventually different oxidization levels can then be managed using biological conditions in the cell.



**Figure 8** Simplified schemas of mitochondria matrix interesting process in the respiration.

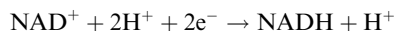
### 3.3. The bio-art of playing with fire (*Electrons source, transport and destination in biological respiration*)

It is well known that respiration is one of the many characteristics of life entities adding to metabolism, reproduction and aptitude to evaluate. Respiration is the main source of energy in the cell, by this way the biological cells can synthesize the needed molecule for growing. In case of the out fundamental state of the cell, oxidative stress under fermentative or semi-fermentative regime, the source of electrons can be different or other new ways are also responsible to offer the requested electrons for uranium reduction (Fig. 7) showing that respiration plays a major way in the cell to reduce ionic form of uranium with possible metabolites which can participate to offer the needed electrons for reduction. It is important to discuss a brief overview of the management of electrons in the cell that creates a veritable bioreactor for nanosynthesis of metallic particles— which is the chemical ability of the cell to biosynthesize, biomineralize and bioreduce ionic element to sculpt the huge amount of nanoparticles.

The respiration consists of exploration of exited electrons by incident photons (in case of plants and microorganisms having a photo system for collection of photon). The exited electrons take a long way in small laps of time including electron transporters proteins to grow up and down in energetic levels in the goal to minimize the quanta of energy; the electrons will then be able to enter in the biosynthesis and metabolism inside the cells. In transport chain of the electrons there are various metallic cofactors that balance the electrons under different energetic levels by shifting the valence first. In order to compare the importance of valence degree of uranium in respiration biological cell at standard condition, iron with its ability to be present at +II and +III valence, can be a theater of different operations using the oxido-reduction reactions, and the electron modulates the energy till it can be then given for other element one by one respecting the global  $\Delta G$  of the system, according to the different valence of this principal metallic transporter of the electron, uranium may get the needed electrons for the biosynthesis of nanoparticles regarding its higher affinity to the electrons. The novel value authorizes the electron to enter in other reaction as some reactive molecular species with oxygen in case of Oxygen respiration or Sulfur when they are the final acceptors of electrons in the whole history of the electrons in case of secondary metabolite formation. In second shifting process the electrons can include different elements and engage the whole atoms in biomolecules and participate for a global biosynthesis. It is from the first mode that the electrons are well explored for the bioreduction of exogenous elements such as uranium in our case. Fig. 8 summarizes the dynamism of the electrons in mitochondria compartment directly related to the respiration which explains that respiration is involved in the bioreduction of metallic ions.

In this close context, in fundamental state of the cell, the collection of the electrons refers to three major possibilities which are available and can be explored. First possibility is that, the electron is directly available from the respiration process. Second, that electron is available from metabolites, as global remaining electrons which prove that plant extract has a capacity of reducing the metallic ions. And the third available source of electrons is the transition of electrons playing

in enzymatic reactions (Zhang et al., 2011). The main key in electrons transport and hydrogen manipulation is done in the mitochondrial matrix by the NADH system and embedded a regenerative system for available electrons, the principle process can be written in the following reaction;



The respiration is the siege to manipulate pH and the balancing of electrons, the pH is well controlled by the reactions which happen in mitochondria matrix and the transmembranous movement of  $\text{H}^+$  as mentioned earlier about the pH is the main controller of uranium different systems coupled with the global potential. Huge oxidoreduction reactions took place and the final electrons' acceptance reaction can be summarized by reduction of water or  $\text{H}_2\text{S}$  gaz:



The cited two reactions given below explain the possibility of the source of available oxygen for uranium formation of oxides forms and potential sulfurous as the highest negativity of these elements.

## 4. Biological assistance synthesis of uranium nanoparticles

The principle to reduce uranium using life entities (microorganisms, plants and plant extract) is based on remaining of electrons from the global metabolic reaction and electronic flow playing essentially in respiration and related phenomena. As uranium can circulate with different valence, its reduction can be done inside the cell via the available electrons. Moreover, it needs a minimum potential to be reduced then the genesis of nucleus which leads to uranium oxide based nanoparticles. The shifted ionic form of uranium is less competitive with respect to oxydo reduction. The obtained nanoparticles, if any, prove that the cell directly uses uranium by balancing it between the different oxydo-reduction potential levels. This manner makes it possible for living entities to domesticate uranium and resolve its highest ability to be reduced.

### 4.1. Bacterial intervention for reduction of uranium

Microorganisms can interact with various metal ions in their environment, which can be beneficial depending on the chemical/physical nature and oxidation state of the metal ion (Kalina et al., 2005). There is a bio-available amount that cell can manage, using physiological pathway. The excess of metal ions involves cells to use their enzymatic equipment to reduce the amount and engage some process to maintain the equilibrium state by adjusting the oxido-reduction balance. There is other advanced process used by cells to discard the oxidation power of some oligoelement the required electrons for reduction, when the concentration becomes so high and the first barrier was crossed. The cell work to synthesize a type of molecule that doesn't react after in terms of oxido-reduction and the power of ionic form will be neutralized definitively. Nanoparticles were synthesized by the biological cell like an alternative and/or an urgent way to resolve a problem of insufficient correction of ions equilibrium, there is difference between ele-

ments and used cells for biosynthesis of nanoparticles. In case of Iron, microorganisms were used and various works show that nanoparticles can be produced at moderated concentration, gold, silver, palladium, and various elements were used to check the capacity of bacteria to manipulate metallic salts (Questera et al., 2013). In case of uranium, the actinide having a great spontaneous radioactivity power with multiple valence states can destroy not only the cell but can modify and destroy each atom on its behind.

Uranium ion can be reduced using bacteria and plants either to get a final particular form, this form can be used for the energetic purpose of uranium, the challenge in this point of view is still based on revelation of various species of microorganisms and plants having this ability. Here we can mention differences between aerobic and anaerobic microorganisms and their capacity to survive under harsh conditions, or a localization of uranium ore regarding a natural leaching or bioassistance leaching called bioleaching of uranium, the same term used by Baranska and Sadowski (2013). To quantify and judge the importance of amount of uranium nanoparticles assimilated in cell scale, there is a small potential quantity produced compared to various ordinary transition metals but in case of this element it has a great value, and the production of a big amount can be assisted by a biomass in case and microorganisms and a whole plants.

Under anaerobic conditions uranium can be complexed with organic ligand like citric acid then it will be reduced to  $U^{(+IV)}$ -citrate. That shows that the organic compound here, which is citric acid, can play a major role in electron donor responsible for uranium bioreduction and immobilization (Baranska and Sadowski, 2013). It is the case of *Clastridium spheroids* bacteria which is able to reduce  $U^{(+VI)}$  to  $U^{(+IV)}$  Francis and Dodge, 2008. The organic model given in this study using citric acid makes the analogy with a huge organic species presenting in the cell representing by the metabolites, then each one can be a citric-acid-like donor of electrons.

Although, uranium can be associated with many other elements in the nature, it can be associated especially with iron and phosphates, the first postulate that can explain the capacity of bacteria and biological living entities to reduce uranium ions, can be the consequence of extraction of the associated element as iron and phosphates because of their important role in metabolism of the cells, by this way the uranium will be associated with oxido-reduction of oxygen and the electronic donor element like sulfates (Lee and Hur, 2014) or nitrates (Bargar et al., 2008).

It is according to the chemical protocols for uranium reducing by the given electrons coming from iron assistance when *Acidithio-bacillus ferrooxidans* the bacteria oxidizes iron from  $Fe^{2+}$  to  $Fe^{3+}$ , the liberating ferric ion reacts with uranium to oxidize the mineral form, then bacteria were used to release uranium from the black schist ore mineral  $U_3O_8$  (Choi et al., 2005), this methodology explains the indirect uses of bacteria to increase the releasing uranium from the natural ore and the bacteria attack for the ore can be sufficient to collect and crowd the small amounts of uranium present in trace quantities even from the radioactive waste that contaminated effluent sediment and water (Baiget et al., 2013). The study given by Loghlin et al. (2003), regarding the reduction of uranium by mixing of iron(II) and iron(III) hydroxides to get  $UO_2$  nanoparticles makes from all bacteria species with  $Fe^{2+}$  and  $Fe^{3+}$  electron transporter systems for balancing charge a

possible nano-manufacture for uranium. The combination of the reduction of Fe and U the becomes possible (Lloyd, 2003) it was shown by Lovley and his coworkers that the bacteria cell of *Geobacter metallireducens* has a capacity to reduce  $Fe(III)$  under anaerobic conditions which get a consequence to reduce  $U(IV)$  Lovley et al., 1991.

In this task it is evident to select natural bacteria or genetically modified ones that can detect a small amount of U and shift it from the ionic form to NPs the condensation of particles in pure agglomerate which can be explored. If some bacteria are able to detect the smallest concentration of the ionic form and shift it to nanoparticles many species are reported it is the case of  $Fe(III)$ -reducing species, *Desulfosporosinus desulfuricans* G20, *Geobacteraceae*. (Wu et al., 2007). Moreover, it is shown that uranium follows the metabolism of iron and the study demonstrates that uranium can be banded with highest affinity with the iron-receptors of the cell especially the transferrin protein tested by Hemadi et al. (2010).

The biological assistance method can be admitted then like an efficacy method of investigation about the presence of uranium and the collection from a groundwater and the ore rocks becomes proper method to domesticate uranium. Many cited bacteria confirm this evidence as some species exist, with the ability to manipulate uranium, it is the case of *Shewanella odenosis* the bacteria which synthesizes  $UO_2$  nanoparticles which aggregates in periplasmic cell space Marshall et al. (2006). Biogenic uranium nanoparticles can be used like shown by Singer et al. (2006) for surface reactivity based on sorption Zn (II) in aqueous solution.

#### 4.2. Natural plant; way for uranium recovery

In agricultural soils, uranium can be in different valence and is enriched by weathering of parent rocks particularly granites (Sasmaz and Yaman, 2008; Makoti et al., 2012) sediments (Qafoku et al., 2014). According to Anke et al. (2009), soils originating from weathered granites like those found in areas where U deposits have been found for producing vegetable forage and food crops. The uranium is available then for plant's uptake at the pH range of 4.0–7.5, and it can circulate at this pH as  $U^{+6}$  in hydrolyzed forms (Meinrath, 1997). Its mobility increases the ability to spread in agricultural soils and increase is taken by the biomass even by assimilation or absorption in case of plants.

The absorption of various metals by plants cannot be selective in the first place as it is governed by the osmotic force to intercalate elements in ionic form. It is only inside the plant parts that exists a strong selection and the segregation of each one, especially according to their valence states, some of them can be used like a mediator transporters of electrons for respiration phenomena or for the secondary metabolism involved in biosynthesis of organic compound of the cell. For some no-usual element like gold, silver and uranium regarding the higher oxido-reduction power a small amount of these elements can be shifted immediately in other form with a low oxidoreduction power it is the same process like shown in previous section, the adequate form is nanoparticles it can differ here by the process used for this reduction. For that uranium can be assimilated by some phanerogams like tomato and wheat (Gulati et al., 1980), the presence of uranium like an additive element at 3.0 ppm, with the standard oligo-element



can be present inside the corps of the plants and uranium uptake by wheat and tomato depends upon the uranium concentration in the soil. The dynamism between the soil and the plant in case of uranium constitute the first gate for the process of manipulation even reduction of the uranium by plants. For the plants having a developed respiration system it is possible that uranium ion interferes with the metal transporter and the reduction can be done at that level, it is also mentioned by Mokhtari et al. (2009) one hypothetical mechanism that explains the reduction of divalent ion reduction related to nitroreductase enzymatic system which implicates an evolution of the electron energetic level till participating to the final given electrons to reduce the ionic form to nanoparticles forms.

The typical example is *Lactuca sativa* uptake of uranium by a natural contamination with uranium in Portugal where the study was done. This study shows that the lettuce tissue was positively correlated with [U] and it was seen in dry plants that uranium was present at different quantities depending on the type of the plant parts, it is from 0.95 to 6 mg/kg in roots and from 0.32 to 2.6 mg/kg in leaves without precision that nanoparticles were synthesized (Neves et al., 2008). Plants having this methodology for assimilation and up-taking can prevent uranium ion from its high chemical capacity to oxidize elements on behalf and switch it in nanoparticles with higher stability.

It is important to think of exploring the species having this ability to reduce spontaneous radioactive elements to nanoparticles and develop application of the whole cell and/or preexistent systems in the cell, especially related to electron flow from electrons source molecule which become an electron fuel-source-like.

## 5. Conclusion

Based on the examples cited in this paper, the possibility to manipulate uranium by biological assistance was revealed. Previously it was known that radioactivity had enough power to destroy and modify the genetic information if the amount of radioactivity is sufficient. Moreover, genetically transformation can modify a creature, which causes serious problems. It is possible in the future, when some kind of harmony was maintain by bio-hybridation of microorganisms with uranium nanoparticles, to get radioactive bacteria which bring more applications. The domestication of some elements introduces new level of exploitation of biogenic uranium and contributes to assimilation of uranium from ore rock. The challenge can be summarized on the effort to make inventories for a species having a capacity to reduce uranium first and the revelation of mechanistic playing in the reduction to energetically consume the final biohybrid uranium. It seems early that we cannot see application of microorganisms having a capacity to reduce uranium and hybridizing in its presence. This way promotes various applications especially with element having a big interest like uranium, not only our interest, but also for a whole family of radioelement and some precious metals.

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